

IN THE SPECIFICATION:

Please amend the paragraph beginning at page 9, line 19, as follows.

--As the example of a method for manufacturing perovskite oxide single crystal, there is the discloser disclosure in the specification of Japanese Patent Application Laid-Open No. 9-188597, in which a process is provided for enabling the perovskite sintered member of $\text{Pb}\left\{(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\right\}\text{O}_3$ (in the aforesaid composition formula, $0 \leq x \leq 0.55$. Pb of 10 mol % or less may be replaced with Ba , Sr , Ca , or the like) to be in contact with seed crystal, and heated at a temperature of 1,000 to 1,450°C in the closed container in the lead atmosphere. However, there is no disclosure of the BaTiO_3 - PbTiO_3 series single crystal having a smaller mol number of Pb than that of Ba . There is also no disclosure as to the effect thereof as a matter of course. Also, when the ratio between the A site and B site of the aforesaid perovskite sintered member is $1.00 > \text{A/B}$, the crystallization speed is remarkably slow. This is the tendency that differs from the present invention as described later.--

Please amend the paragraph beginning at page 11, line 16, as follows.

--It is preferable for the BaTiO_3 - PbTiO_3 series single crystal of the invention that the rearrangement density is 10^2 pieces/cm² or more and 10^6 pieces/cm² or less, and the ratio of pore content is within a range of 1 volume ppm or more and 5 volume % or less. In this way, the BaTiO_3 - PbTiO_3 series single crystal of the invention makes the dielectric loss smaller, and the electromechanical coupling coefficient larger. For example, the dielectric loss is 1 % or less, and the electromechanical coupling coefficients coefficient exceeds 85 %.--

Please amend the paragraph beginning at page 13, line 18, and ending at page 14, line 18, as follows.

--Also, the method of the present invention for manufacturing BaTiO_3 - PbTiO_3 series single crystal comprises the step of single-crystallizing BaTiO_3 - PbTiO_3 compact powder member or sintered member having a smaller Pb -containing mol number than Ba -containing mol number by defining the range of the mol ratio of elements contained therein to be $0.9800 < (\text{Ba} +$

Pb) / Ti < 1.0000, and by heating, while keeping the powder or substance in non-molten condition. More preferably, the range of the mol ratio of elements contained in the compact powder member or sintered member is defined to be $0.9900 < (\text{Ba} + \text{Pb}) / \text{Ti} < 1.0000$. Still more preferably, the range of the mol ratio of elements contained in the compact powder member or sintered member is defined to be $0.9950 \leq (\text{Ba} + \text{Pb}) / \text{Ti} \leq 0.9999$. By heating the BaTiO_3 - PbTiO_3 compact powder member or sintered member having a smaller Pb-containing mol number than Ba-containing mol number, while keeping it in non-molten condition, the reproducibility of single crystal growth is enhanced as compared with the same process of only the BaTiO_3 , BaTiO_3 compact powder member or sintered member that does not contain PbTiO_3 , thus making it possible to manufacture the stable BaTiO_3 - PbTiO_3 series single crystal. Further, by defining the mol ratio of elements contained in the BaTiO_3 - PbTiO_3 series single crystal within a specific range, the crystal growing speed of BaTiO_3 - PbTiO_3 series single crystal becomes faster.--

Please amend the paragraph beginning at page 16, line 3, and ending at page 17, line 1, as follows.

--Further, the method of the present invention for manufacturing BaTiO_3 - PbTiO_3 series single crystal comprises the steps of preparing BaTiO_3 series single crystal or BaTiO_3 - PbTiO_3 series single crystal as seed crystal; coupling BaTiO_3 - PbTiO_3 series sintered member composed of crystal grain of average granular diameter of $20 \mu\text{m}$ or less, having the relative density of 95% or more, with the {100} plane, {110} plane, or {111} plane of the seed crystal; and single-crystallizing by heating, while keeping the coupled substance in non-molten condition. More preferably, the mol ratio of elements contained in the BaTiO_3 - PbTiO_3 compact powder member or sintered member is within a range of $0.9950 \leq (\text{Ba} + \text{Pb}) / \text{Ti} \leq 0.9999$. In the method of the invention for manufacturing BaTiO_3 - PbTiO_3 series single crystal, the single crystallization takes place stably from the coupling portion between the compact powder member or sintered member and the seed crystal by use of the BaTiO_3 - PbTiO_3 compact powder member or sintered member coupled with the seed crystal in the aforesaid condition, and the

reproducibility of single crystal growth is enhanced. Also, if the mol ratio of elements contained in the aforesaid compact powder or sintered member is within the designated range, the crystal growing speed of BaTiO₃ - PbTiO₃ series single crystal becomes faster still.

Please amend the paragraph beginning at page 18, line 14, and ending at page 19, line 11, as follows.

--The BaTiO₃ - PbTiO₃ series single crystal of the present invention is single-crystallized by heating BaTiO₃ - PbTiO₃ compact powder member or sintered member having a smaller Pb-containing mol number than Ba-containing mol number, while keeping the powder or substance in non-molten condition. The effect of the reproducibility of the crystal growth of the present invention cannot be demonstrated even if the method of manufacture thereof is applied to the compact powder member or sintered member composed of only BaTiO₃. Although the mechanism thereof has not been confirmed as yet, it is inferred as given below. When the BaTiO₃ - PbTiO₃ compact powder member or sintered member is heated, while kept in non-molten condition, lead or lead compound is evaporated from the surface of the powder or signatured substance, and externally dispersed, and the deficiency of lead ~~ensues on~~ ensues on the surface of the compact powder member or sintered member. Thus, lead shifts from the inside of the compact powder member or sintered member to the surface to compensate for the deficiency thereof. At this juncture, the granular interface in the ~~inside of~~ the compact powder member or sintered member tends to move easily, hence enabling the crystal growth to occur stably.--

Please amend the paragraph beginning at page 27, line 1, and ending at page 28, line 2, as follows.

--However, when manufacturing the BaTiO₃ - PbTiO₃ series single crystal the ratio of PbTiO₃ content of which exceeds 30 mol %, the lead evaporation becomes particularly conspicuous to make it easier to change the composition from the target one. Further, the ratio of pore content of the obtained single crystal tends to become higher. In order to suppress the lead

evaporation, there are often the cases where only the execution of the heating process under the lead atmosphere as described earlier is not good enough. For example, it is preferable to execute the heating process in a pressurized container under a pressure of more than one atmosphere. There is a need for a comparatively long period of heating process (10 hours or more) when a single crystal synthesis is executed by the sintering method using such a pressurized container as HIP. As compared with the precess process under the normal pressure, this is unfavorable in terms of the productivity and costs. For the BaTiO₃ - PbTiO₃ series single crystal of the present invention, it is desirable to provide the rearrangement density of 10² pieces/cm² or more and 10⁶ pieces/cm² or less, and the ratio of pore content of 1 volume ppm or more and 5 volume % or less. In this way, the single crystal of the present invention presents a small dielectric loss, and a large electromechanical coupling coefficient. For example, the dielectric loss is 1 % or less, and the electro-mechanical coupling coefficient exceeds 85 %.--

Please amend the paragraph beginning at page 28, line 22, and ending at page 30, line 3, as follows.

--Also, it is possible to use the mixture of BaTiO₃ and PbTiO₃, which are is obtainable by the wet or hydro-thermal method, such as coprecipitation or oxalic acid method, and also, BaTiO₃ - PbTiO₃ powder or the like, which is obtainable by the wet, hydrothermal method, such as coprecipitation or oxalic acid method, among some others. For the material powder, it is desirable to keep the average granular diameter of the primary grain to be within a range of 0.055 μm . Also, as described earlier, it is preferable to adjust the material powder so that the mol ratio of the elements contained in the BaTiO₃ - PbTiO₃ compact powder member or sintered member, which is obtained from such material power to become the starting substance, should be $0.9800 < (\text{Ba} + \text{Pb}) / \text{Ti} < 1.0000$. Also, more preferably, the material powder is adjusted so that the mol ratio of the elements contained in the BaTiO₃ - PbTiO₃ compact powder member or sintered member should be $0.9900 < (\text{Ba} + \text{Pb}) / \text{Ti} < 1.0000$. Still more preferably, it should be $0.9950 \leq (\text{Ba} + \text{Pb}) / \text{Ti} \leq 0.9999$. The composition-adjusted powder is made to be the compact powder member after the general formation by means of a uniaxial press or a cold press

using hydrostatic pressure. The compact powder member thus obtained may be made a sintered member by sintering under the normal condition. The compact powder member or sintered member is heated in the non-molten condition to obtain the bulky crystal grain of the BaTiO₃ - PbTiO₃ series single crystal having the average granular diameter of 1 mm or more. The heating in the non-molten condition is given more preferably within a temperature range of 1,200°C or more and 1,400°C or less. Further, using the single crystal thus obtained by the aforesaid method as seed crystal it may become comparatively easy to make large BaTiO₃ - PbTiO₃ series single crystal.--

Please amend the paragraph beginning at page 30, line 25, and ending at page 32, line 11, as follows.

--Also, when the single crystallization is executed using the seed crystal, the mol ratio of the elements contained in the BaTiO₃ - PbTiO₃ series sintered member to be single-crystallized should preferably be adjusted to be $0.9800 < (Ba + Pb) / Ti < 1.0000$. More preferably, the mol ratio should be adjusted to be $0.9900 < (Ba + Pb) / Ti < 1.0000$. Still more preferably, it should become $0.9950 \leq (Ba + Pb) / Ti \leq 0.9999$. Further, the sintered member is sintered so that the average granular diameter of the crystalline grain should be 20 μm or less, and the relative density should be 95 % or more. The sintering method is not particularly limited, and the normally pressurized sintering, the hot press, the HIP (hot isostatic press), or the like is applicable here. In this respect, if the ratio of pore content of the sintered member exceed 5 volume %, the ratio of pore content in the single crystal obtained by the crystal growth is also increased, which unfavorably lowers the mechanical strength thereof. With the composition having a large amount of lead in particular, the ratio of pore content tends to become greater due to the lead evaporation during the growth of single crystal. In this case, therefore, it is preferable to keep the ratio of pore content in the sintered member to be less than 5 volume %. It is also preferable to precisely polish the coupling surface of the sintered member and seed crystal to be the surface roughness $Ra = 1.0 \text{ nm}$ or less, and the flatness $\lambda (\lambda = 633 \text{ nm})$ or less, respectively. The polished surfaces of the sintered member and seed crystal may be in contact directly or may

be in contact after coating the organic or inorganic acid that contains Ba, Pb, Ti component. The seed crystal and sintered member, the polished surfaces of which are in contact with each other, should preferably be coupled by heating for a specific time with self-weight or a load of approximately 9.8 MPa or less. Further, it is more preferable to execute the coupling in the lead atmosphere in order to suppress the lead evaporation from ~~neat~~ near the surface of the sample in the coupling process.--

Please amend the paragraph beginning at page 34, line 14, as follows.

--Also, the rearrangement in single crystal can be observed using a microscope or the like as etch pit (= ~~rearrangement~~ rearrangement) by corroding the crystalline surface of the single crystal with HCl - HF solution or the like. In detail, the number of rearrangement (etch pit) generated in several hundreds to thousand μm^2 is counted and the counted number is changed to per ~~1cm²~~ 1 cm² in order to determine the rearrangement density.--

Please amend the paragraph beginning at page 44, line 10, as follows.

--From this result, it has been found that the growing speed is 0.90 mm/h, and that the growth is possible at a speed faster than the growing speed indicated in the second embodiment. Also, the Pb density of the surface layer of the sample of the single crystal of BaTiO₃ of 93.0 mol % - PbTiO₃ of 7.0 mol %, which is obtained by the sintering method, has almost no difference with the Pb density in the central portion, and it has been found that the ~~simple~~ sample is composed uniformly as a whole. The ratio of pore content is 0.4 volume % in the single crystal of BaTiO₃ of 93.0 mol % - PbTiO₃ of 7.0 mol %, using the seed crystal, and the rearrangement density is found to be $5 \times 10^2 / \text{cm}^2$ when examined by etching it in the HCl - HF solution.

(Eighth Embodiment)--

Please amend the paragraph beginning at page 46, line 6, as follows.

--From this result, it has been found that the growing speed is 0.70 mm/h, and that the growth is possible at a speed much faster than the growing speed of the conventional melt solidification method. Also, the ratio of pore content is 0.2 volume % in the single crystal of BaTiO₃ of 93.2 mol % - PbTiO₃ of 6.8 mol %, which is obtained by the sintering method using the seed crystal, and the rearrangement density is found to be $\pm 10^3 / \text{cm}^2$ $1 \times 10^3 / \text{cm}^2$ when examined by etching it in the HCl - HF solution.

(Ninth Embodiment)--

Please amend the paragraph beginning at page 51, line 20, and ending at page 52, line 9, as follows.

--From this result, it has been found that the growing speed is 0.47 mm/h, and that the growth is possible at a speed much faster than the growing speed of the conventional melt solidification method. Also, the ratio of pore content is 0.8 volume % in the single crystal of BaTiO₃ of 99.5 mol % - PbTiO₃ of 0.5 mol %, which is obtained by the sintering method using the seed crystal, and the rearrangement density is found to be $2 \times 10^2 / \text{cm}^2$ when examined by etching it in the HCl - HF solution. FIG. 3 shows the result of measurement of the sample by means of X-ray diffraction (before single crystallization), and FIG. 4 shows the result thereof (after single crystallization). (In FIG. 4, two ~~peeks~~ peaks are observable in the vicinity of $2\theta = 45^\circ$. This is because the X-ray of target own is separated into $K\alpha_1$ and $K\alpha_2$.)

(Twelfth Embodiment)--

Please amend the paragraph beginning at page 60, line 8, and ending at page 61, line 19, as follows.

--BaTiO₃ (Ba / Ti = 1.0000) and PbTiO₃ (Pb / Ti = 1.0100) powder is prepared by the coprecipitation method, and blended in a ration of 90.0 mol : 10.0 mol. While being crashed crushed by means of hot mill, this blended powder is formed into a disc (of 16 mm diameter). For the compact powder member thus formed, the mol ratio of contained elements is (Ba + Pb) / Ti = 1.0010. This powder is sintered at 1,350°C for 10 hours to obtain the sintered member of

BaTiO₃ of 90.0 mol % - PbTiO₃ of 10.0 mol %. The sintered member thus obtained is composed of minute crystal grain of average granular diameter of approximately 3 μm , thus making it impossible to obtain the single crystal in a size sufficient enough to be used as seed crystal. Therefore, as in the case of the first comparative example, the BaTiO₃ series single crystal, which is grown by means of the TSSG method and made available on the market, is used as the seed crystal. On the other hand the same compound is formed into a disc of 10 mm diameter \times 15 mm thick, and sintered at 1,250°C for three hours to obtain the sintered member of BaTiO₃ of 90.0 mol % - PbTiO₃ of 10.0 mol % in the relative density of 97.8%. The mol ratio of elements contained in this sintered member is (Ba + Pb) / Ti = 1.0010. The end face of this sintered member is mirror finished to be the surface roughness Ra = 0.4 nm and the flatness $\lambda/6$ as in the first comparative example. The polished surfaces of both seed crystal and sintered member are rinsed using acetone for coupling by coating a mixed solution of BaCl₃ and TiOCl₂ (mixing ratio: 1 : 1) on the coupling interface. While maintaining this state, these are retained at 1,390°C for 30 hours in the non-molten condition for the execution of single crystallization. After this growing process, it is found that almost no single crystallization has taken place, but only in a width of approximately 1 to 2 grain (approximately 5 to 10 μm) from the surface coupled with the seed crystal.

(Third Comparative Example)--

Please amend the paragraph beginning at page 61, line 20, and ending at page 62, line 22, as follows.

--BaTiO₃ - PbTiO₃ series single crystal is grown by means of the TSSG method. As the material of solution, the BaTiO₃ powder, TiO₂ powder, and PbTiO₃ powder, which are available on the market, are used. The sintered member is prepared using the material powder in a mol ratio of BaTiO₃ : TiO₂ : PbTiO₃ = 1 : 0.5 : 0.01. This sintered member is placed in a platinum crucible to melt the material by means of high-frequency induction heating. The growing temperature is 1,440°C. The BaTiO₃ seed crystal of <100> orientation, which is fixed to the platinum holder, is immersed in this solution, and the temperature is decreased at 0.4°C/h

along with the rotation of 30 rpm, and the crystallization is performed by a speed of 0.1 mm/h. After approximately 200 hours, the drawing-up terminates when the temperature reaches 1,330°C (eutectoid temperature). The crystal thus obtained is 25 mm diameter and 16 mm long (volume: 7.9 cm³). ~~The~~ The inside of the crystal is of porous structure (the ratio of pore content: 8 volume %) having many numbers of voids of several μm to several tens of μm created along with the Pb evaporation on the way of growth. With a microscope, the occurrence of many inclusions other than perovskite phase is observed. The rearrangement density in the crystal is $2 \times 10^6 / \text{cm}^2$. It is larger than the rearrangement density of the BaTiO₃ - PbTiO₃ series single crystal of the present invention. Also, the productivity is only 0.04 cm³/h, which is approximately 1/100 as compared with the productivity of the BaTiO₃ - PbTiO₃ series single crystal of the present invention.--

Please amend the paragraph beginning at page 66, line 8, as follows.

--For the liquid discharge head 11 structured as described above, the piezoelectric type actuator 19 is driven to press liquid in the corresponding liquid chamber 13 when driving signals are applied from outside to the piezoelectric type actuator 19, and liquid is discharged as liquid droplet from the liquid discharge port 12 communicated with the liquid chamber 13.--